Supporting Information

Thiol-Ene Photopolymerization of Vinyl-Functionalized Metal-Organic Framework towards Mixed-Matrix Membranes

Chinnadurai Satheeshkumar,[a,†] Hyun Jung Yu,[b,†] Hyojin Park,[c,†], Min Kim,*[c] Jong Suk Lee,*[b] Myungeun Seo*[a,d]

[a]Graduate School of Nanoscience and Technology, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Korea

[b]Department of Chemical and Biomolecular Engineering, Sogang University, Seoul 04107, Korea

[c]Department of Chemistry and BK21Plus Research Team, Chungbuk National University, Cheongju 29644, Korea

[d]Department of Chemistry, KAIST, Daejeon 34141, Korea

[†]C.S., H.J.Y., and H.P. equally contributed to this work.

*To whom should be addressed: minkim@chungbuk.ac.kr (M.K.); jongslee@sogang.ac.kr (J.S.L.); seomyungeun@kaist.ac.kr (M.S.)

This information includes:

Supporting Table S1

Supporting Figures S1 – S13

Appendix

Table S1. Composition of MMMs synthesized in this study

Entry	Sample	UiO-66-CH=CH_2 loading[a] ($wt\%_{Expt}$)	UiO-66-CH=CH_2 loading ($wt\%_{theo}$)	Polymer matrix[b] (wt%)
1	MMM(0)	0	0	100
2	MMM(60%)	61	60	40
3	MMM(50%)	51	50	50
4	MMM(35%)	36	35	65

[a]Experimental loading calculated by TGA meaurements.
[b]weight ratio of PEO-250, PETM, and EDDT in the polymerization mixture was fixed as PEO-250:PETM:EDDT = 54:26:20.

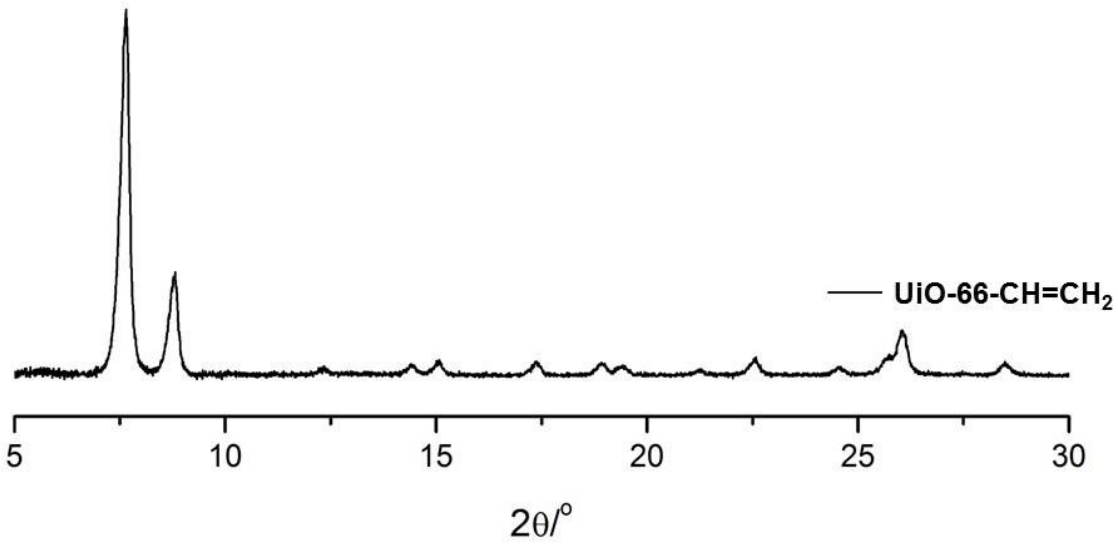


Figure S1. PXRD pattern of UiO-66-CH=CH_2.

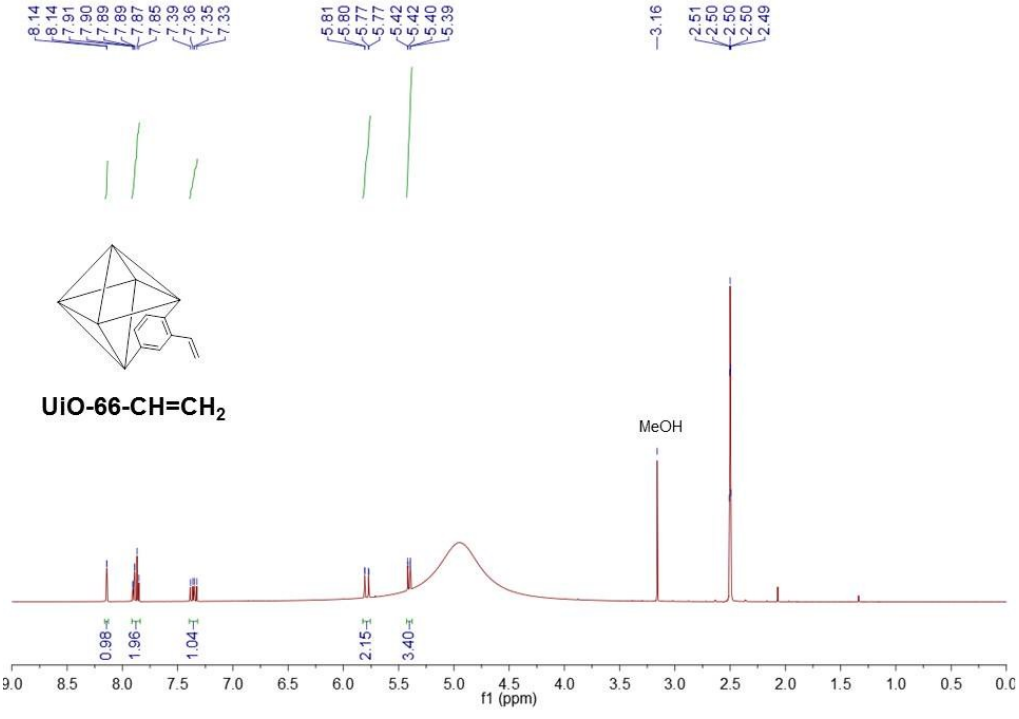


Figure S2. ^{1}H NMR of UiO-66-CH=CH_2 after acid digestion.

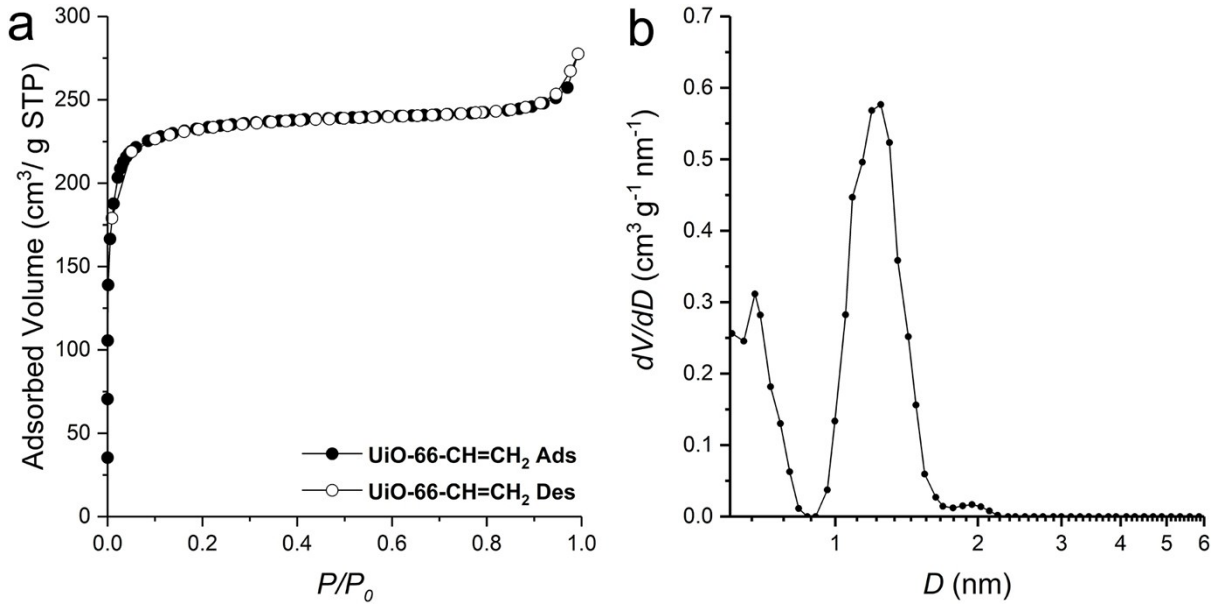


Figure S3. (a) N_2 sorption isotherm of UiO-66-CH=CH_2 obtained at 77 K. (b) Pore size distribution of UiO-66-CH=CH_2 estimated by non-local density function theory (NLDFT) analysis of the adsorption branch of the nitrogen sorption isotherm.

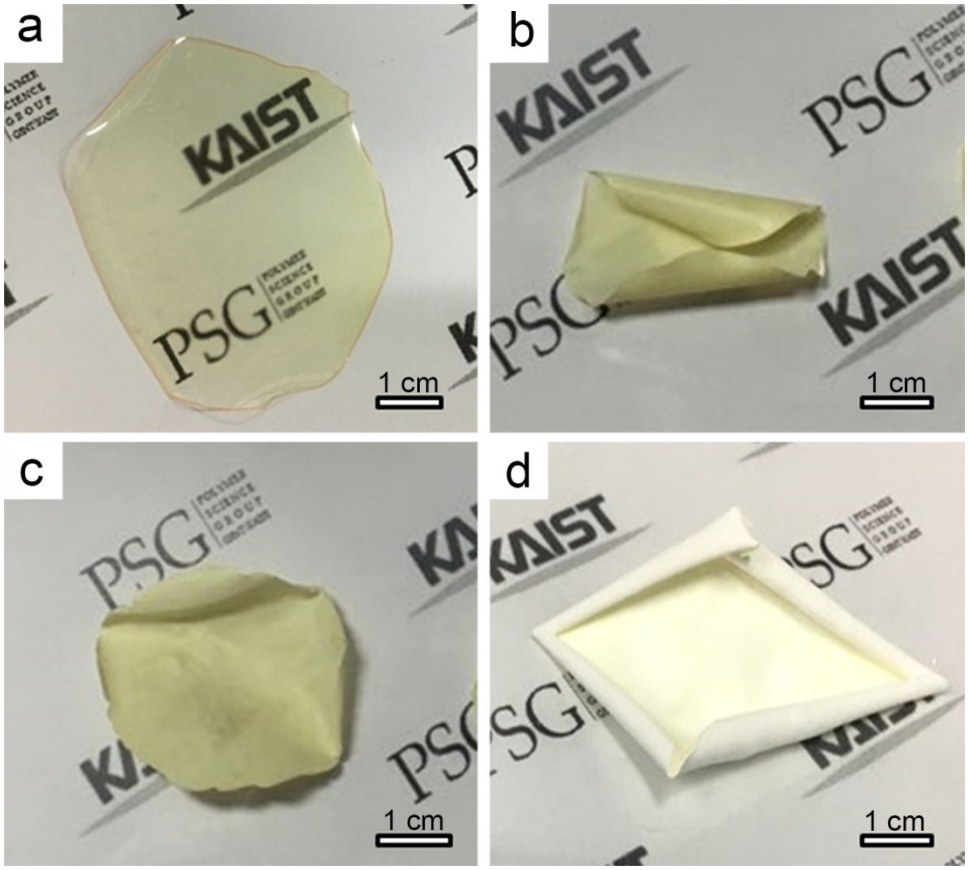


Figure S4. Photographs of free-standing (a) MMM(0), (b) MMM(35%), (c) MMM(50%) and (d) MMM(60%). A scale bar corresponds to 1 cm.

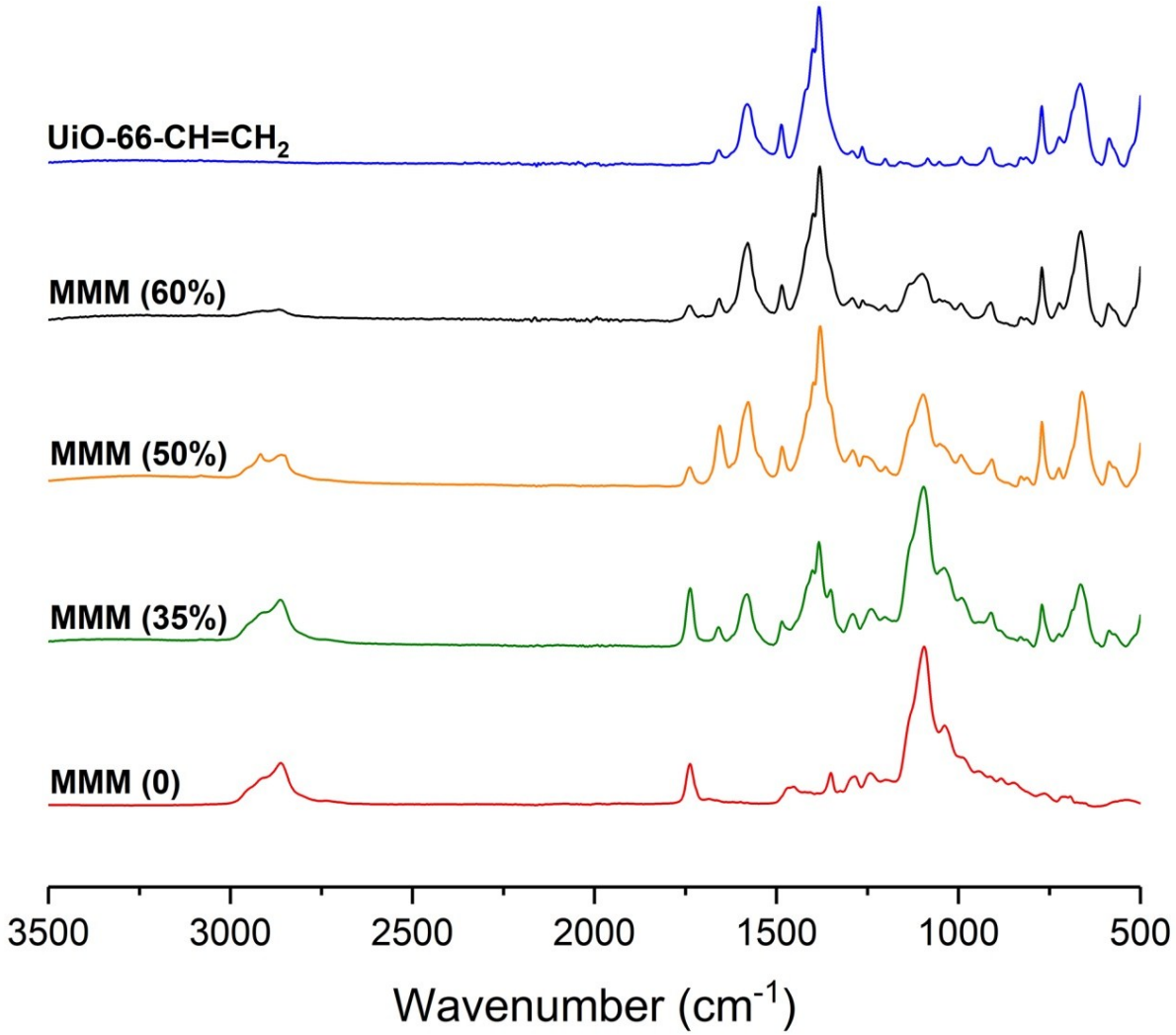


Figure S5. FTIR spectra of MMM(0), MMM(35%), MMM(50%), and MMM(60%) in comparison with UiO-66-CH=CH_2.

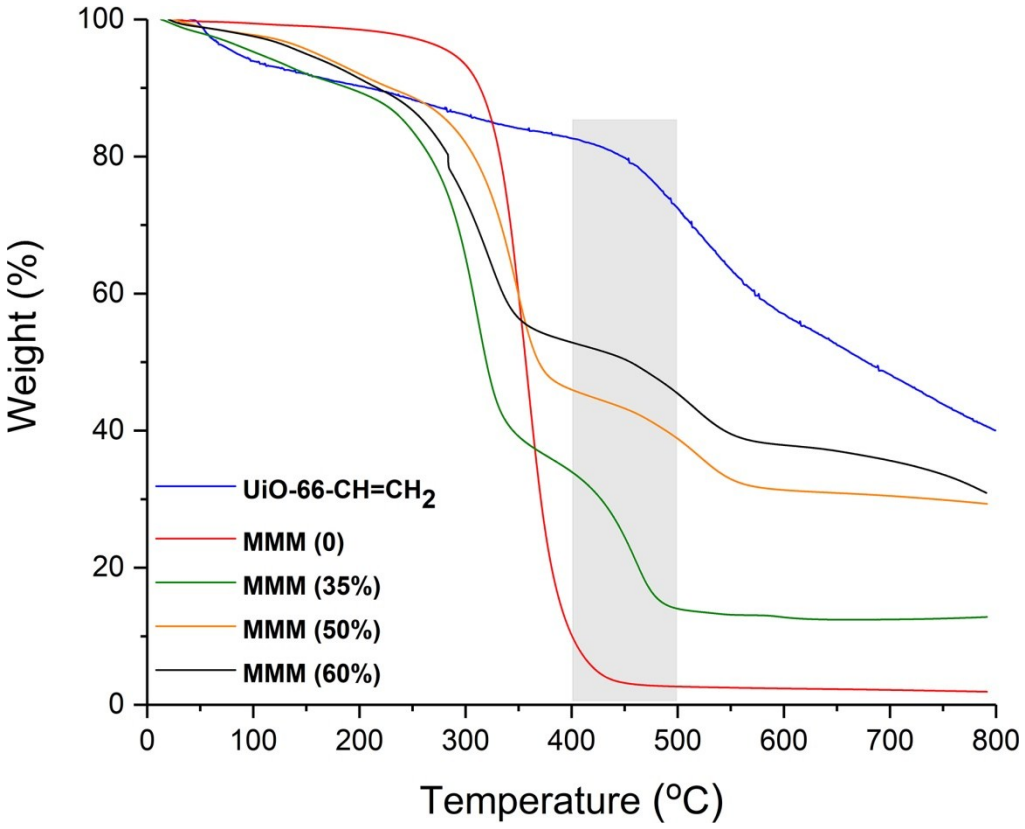


Figure S6. TGA analysis of MMM(0), MMM(35%), MMM(50%), MMM(60%) in comparison with UiO-66-CH=CH_2 (the gray color region is used to calculate the experimental composition of filler, see Table S1).

Calculation of experimental loading of filler by TGA measurement: (see the Table S1)

Let us consider,

$wt\%_{filler} + wt\%_{polymer\ matrix} = 1$

$wt\%_{polymer\ matrix} = 1 - wt\%_{filler}$ ……(a)

Residual $wt\%_{filler,\ TGA}$ = (loss of $wt\%_{filler,\ TGA}$ x $wt\%_{filler}$) + (loss of $wt\%_{polymer\ matrix,\ TGA}$ x $wt\%_{polymer\ matrix}$) …… (b)

Apply equation a into b

= (loss of $wt\%_{filler,\ TGA}$ x $wt\%_{filler}$) + (loss of $wt\%_{polymer\ matrix,\ TGA}$ (1-$wt\%_{filler}$) …… (c)

where,
loss of $wt\%_{filler,\ TGA}$ is 80%
loss of $wt\%_{polymer\ matrix,\ TGA}$ is 3%

Apply this value into equation (c)

Residual $wt\%_{filler,\ TGA}$ = 80% x $wt\%_{filler}$) + 3%(1 – $wt\%_{filler}$) …… (d)

where,
Residual $wt\%_{filler,\ TGA}$ are 30.5%, 42.7% and 50.2% for MMM(35%), MMM(50%) and MMM(60%), respectively (indicated as gray color background in Figure S6)

- MMM(35%)
  30.5% = 77% x $wt\%_{filler}$ + 3%
  $Wt\%_{filler}$ = 36%

- MMM(50%)
  42.7% = 77% x $wt\%_{filler}$ + 3%
  $Wt\%_{filler}$ = 51%

- MMM(60%)
  50.2% = 77% x $wt\%_{filler}$ + 3%
  $Wt\%_{filler}$ = 61%

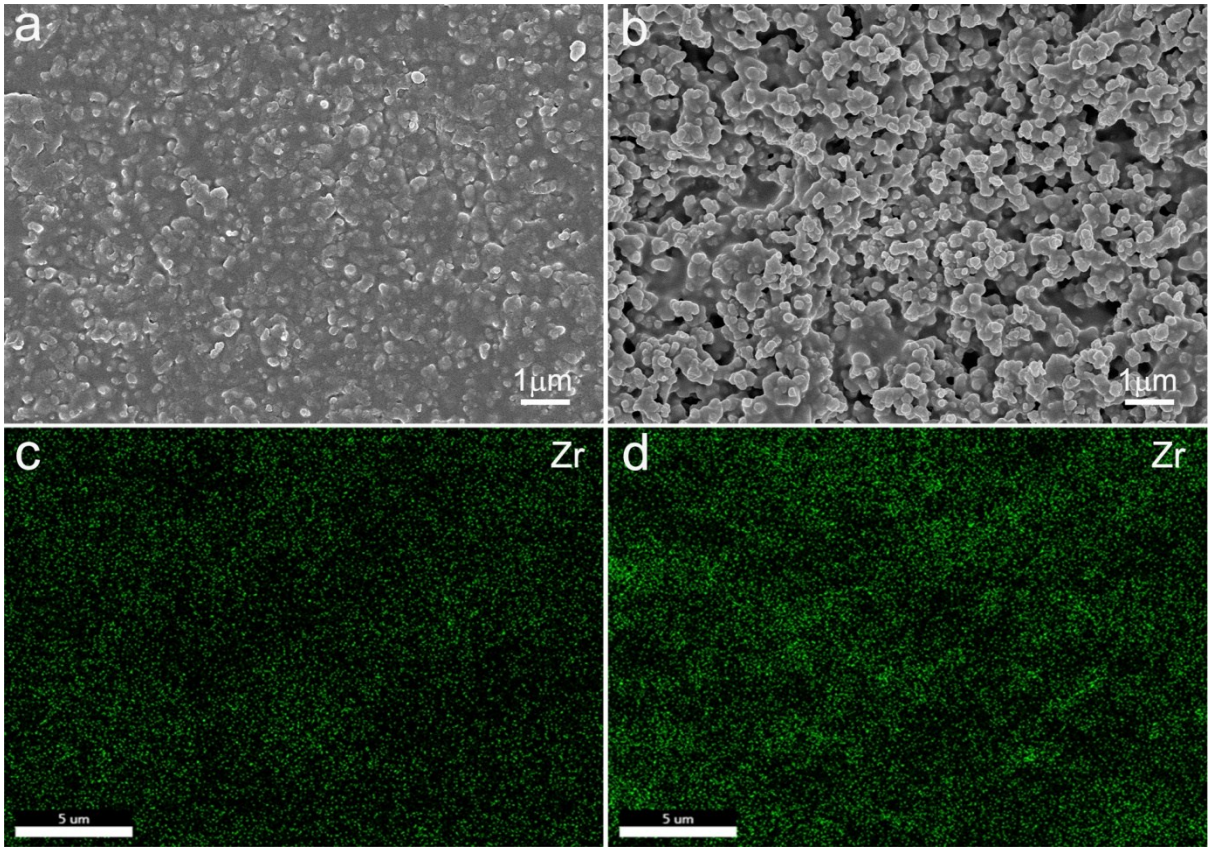


Figure S7. SEM images (a and b) and EDS data (c and d) of MMM(35%) (a and c) and MMM(60%) (b and d).

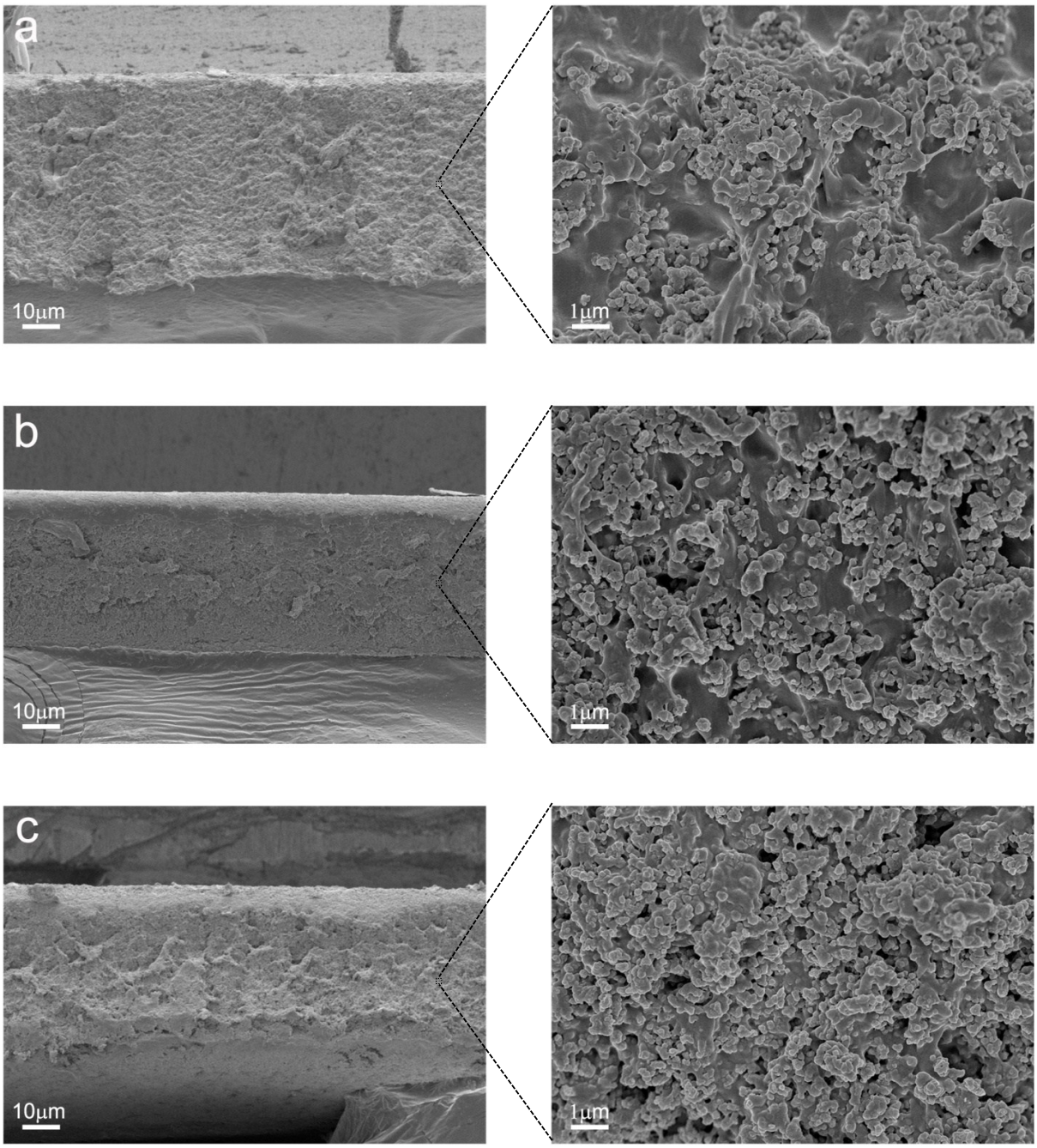


Figure S8. Cross-sectional SEM images of MMMs. (a) MMM(35%). (b) MMM(50%). (c) MMM(60%).

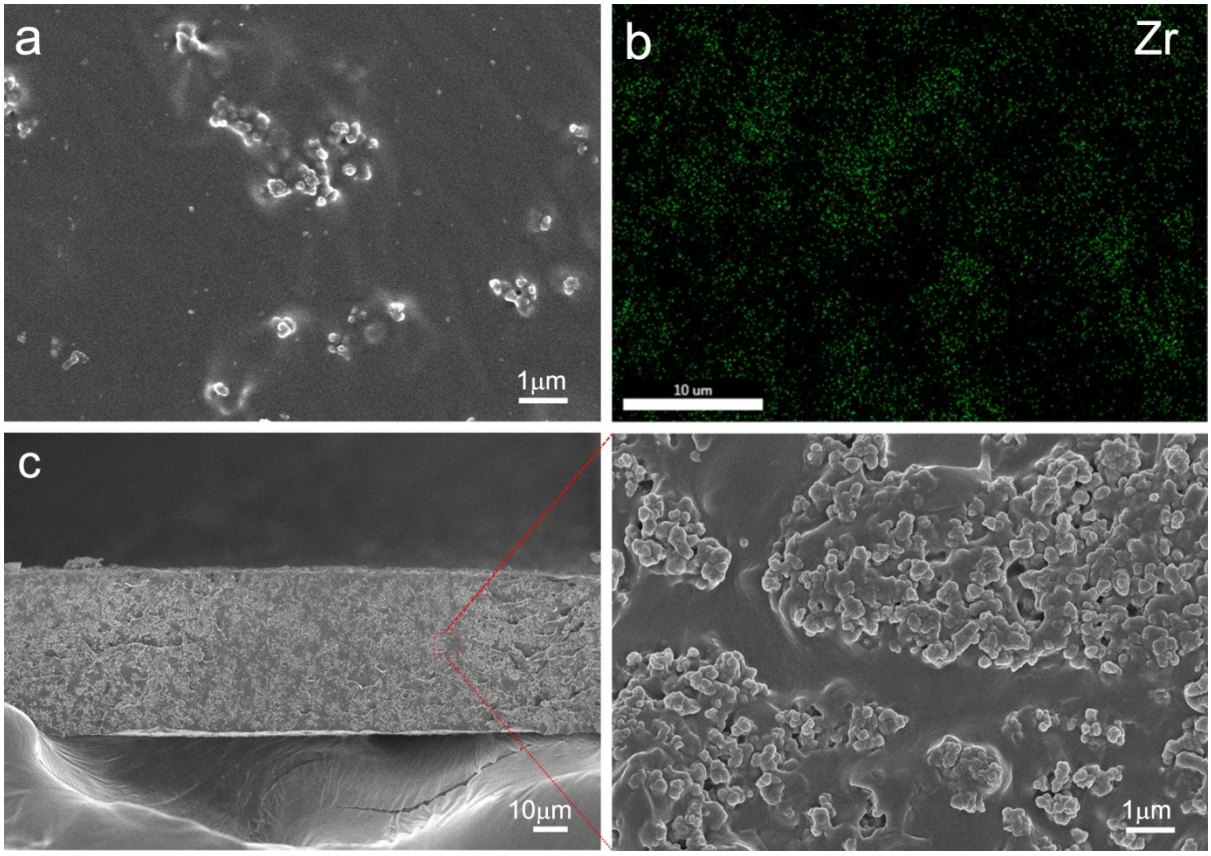


Figure S9. MMM prepared from 20 wt% of pristine UiO-66 (without the vinyl functionality). (a) SEM image of the surface. (b) Corresponding EDS data. (c) Cross-sectional SEM images.

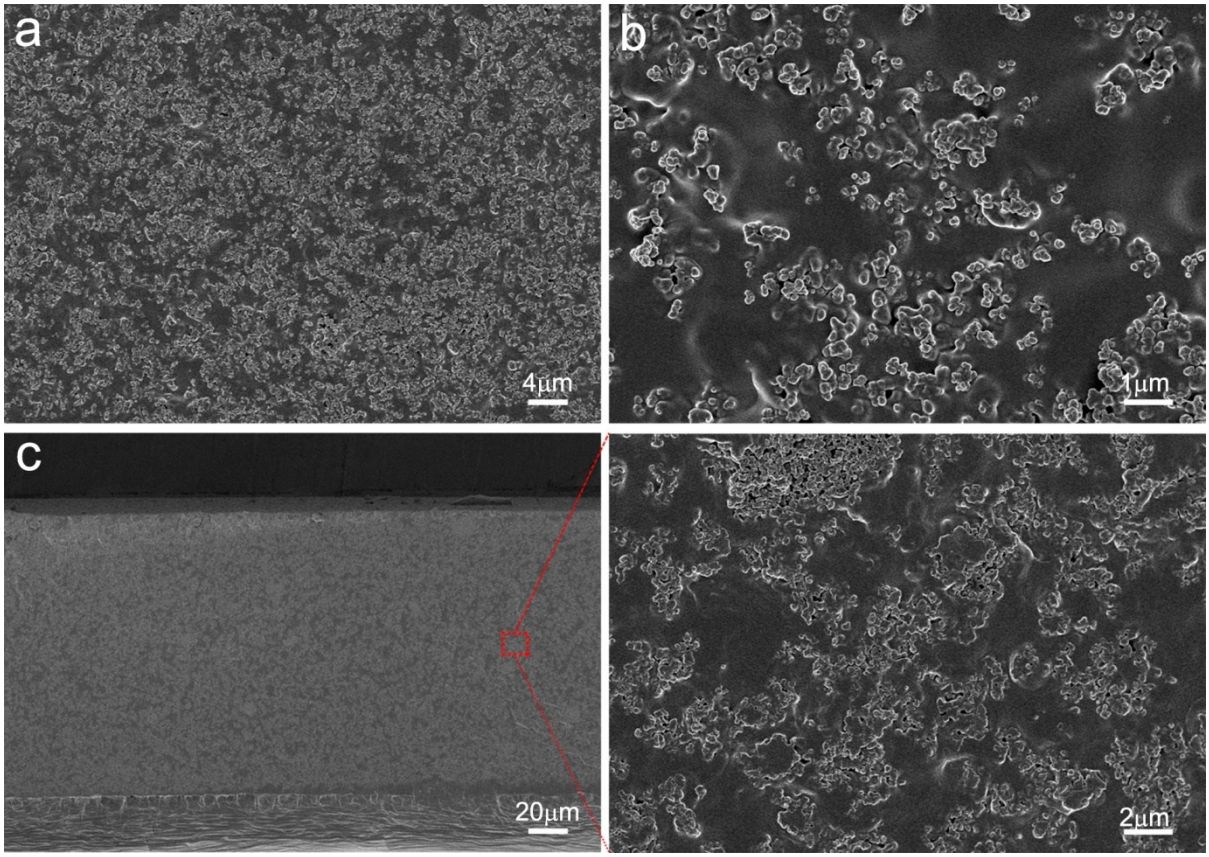


Figure S10. MMM prepared from 35 wt% of pristine UiO-66 (without vinyl functionality). (a and b) SEM images of the surface at different scale bar. (c) Cross-sectional SEM imges.

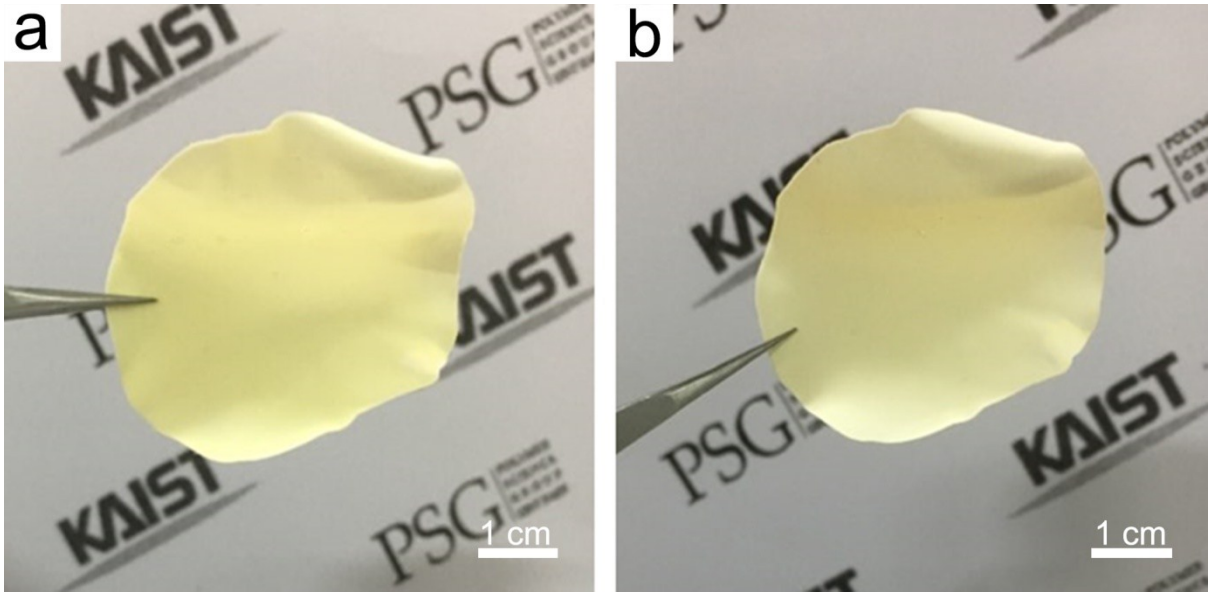


Figure S11. Photographs of free-standing MMM(50%) before (a) and after (b) soaking in DMF for 1 h at room temperature.

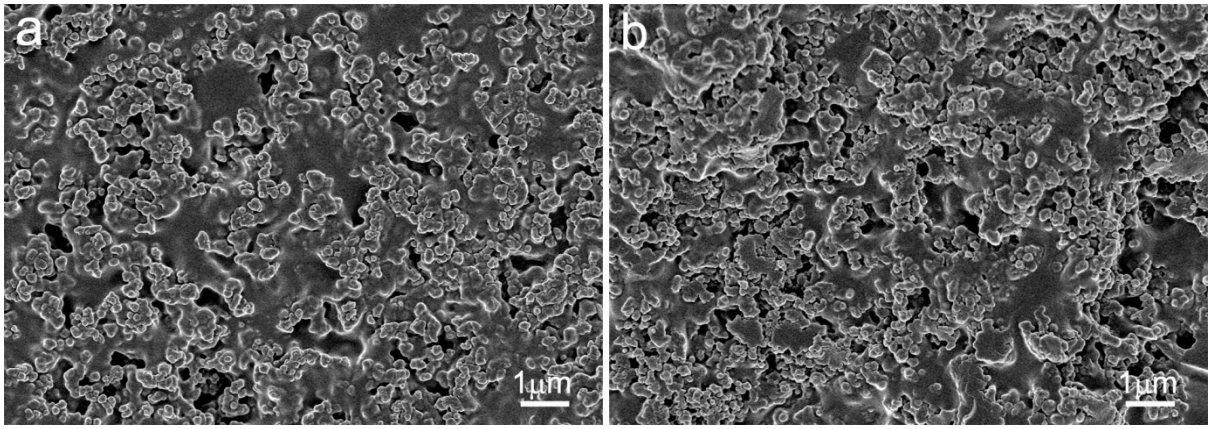


Figure S12. Surface (a) and cross-sectional (b) SEM images of MMM(50%) after the soaking in DMF for 1 h at room temperature.

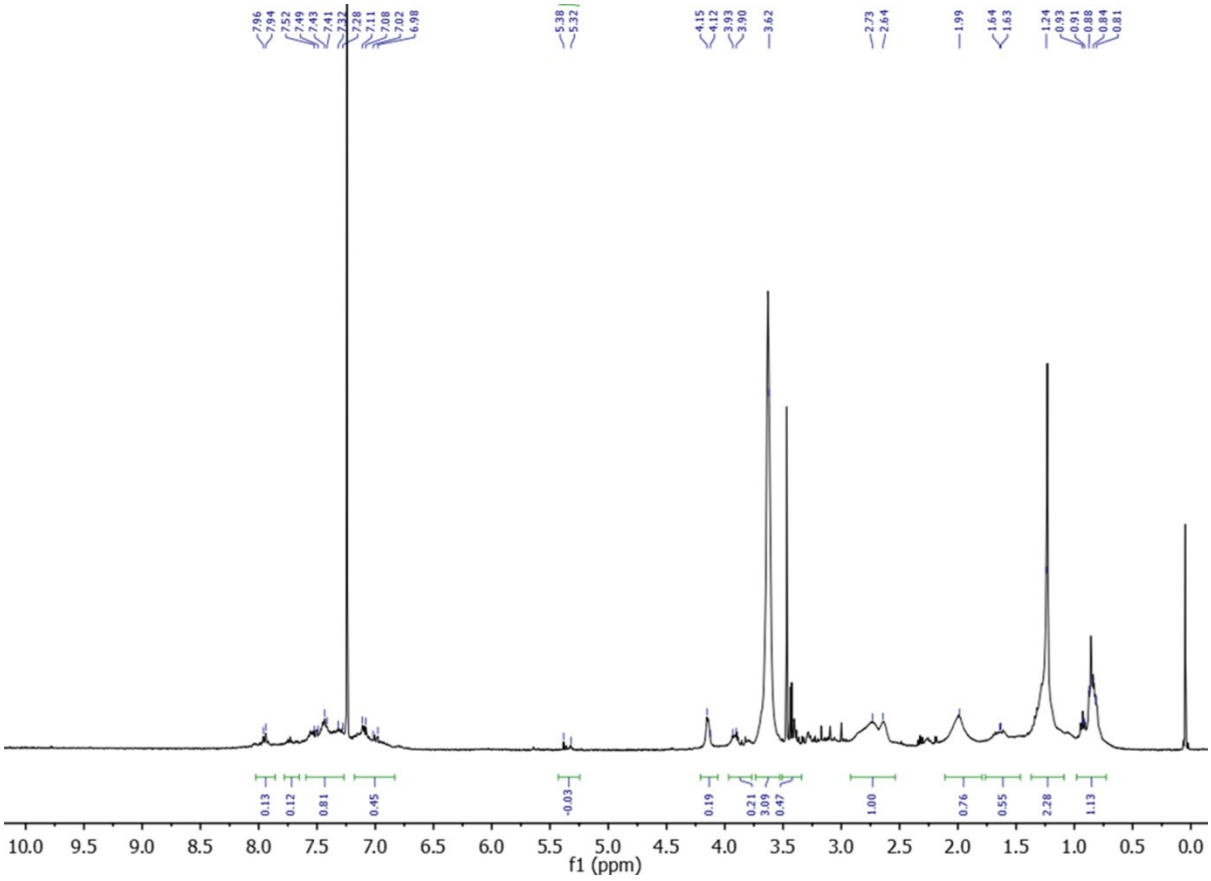
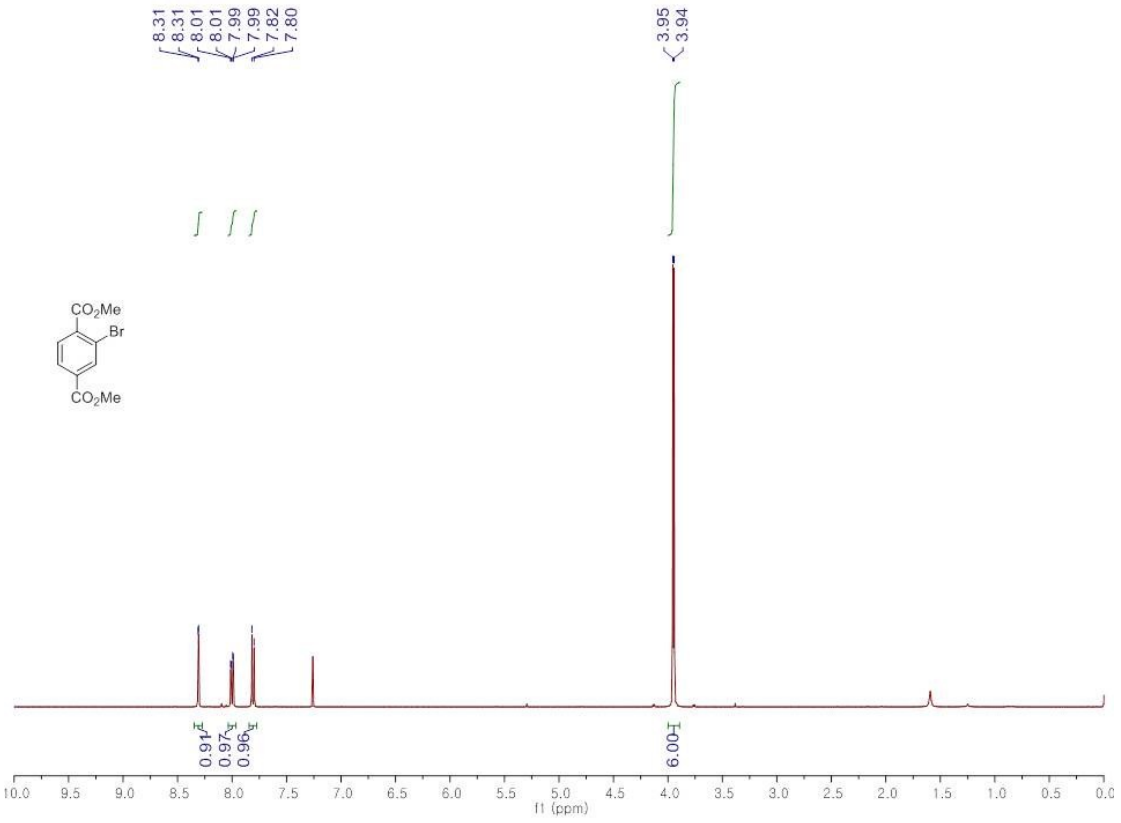


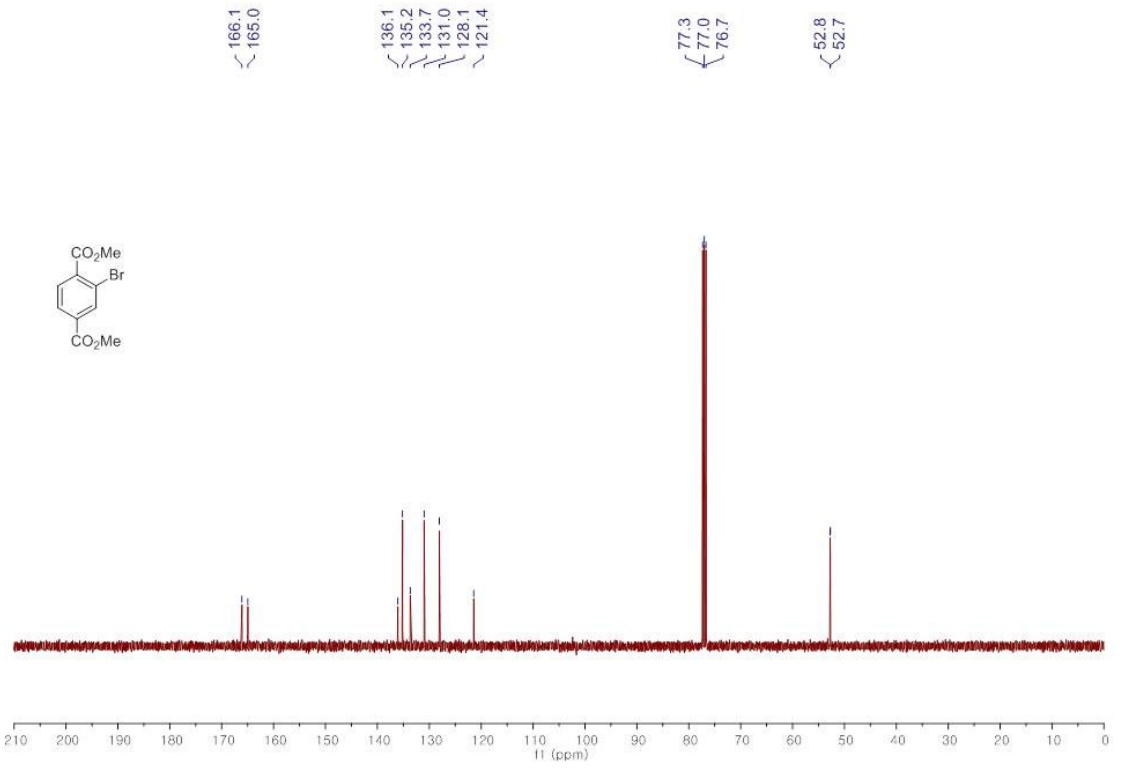
Figure S13. ^{1}H NMR spectrum of (400 MHz, $CDCl_3$) of the concentrated sol fraction obtained by immersing MMM(50%) in DMF.

Appendix.

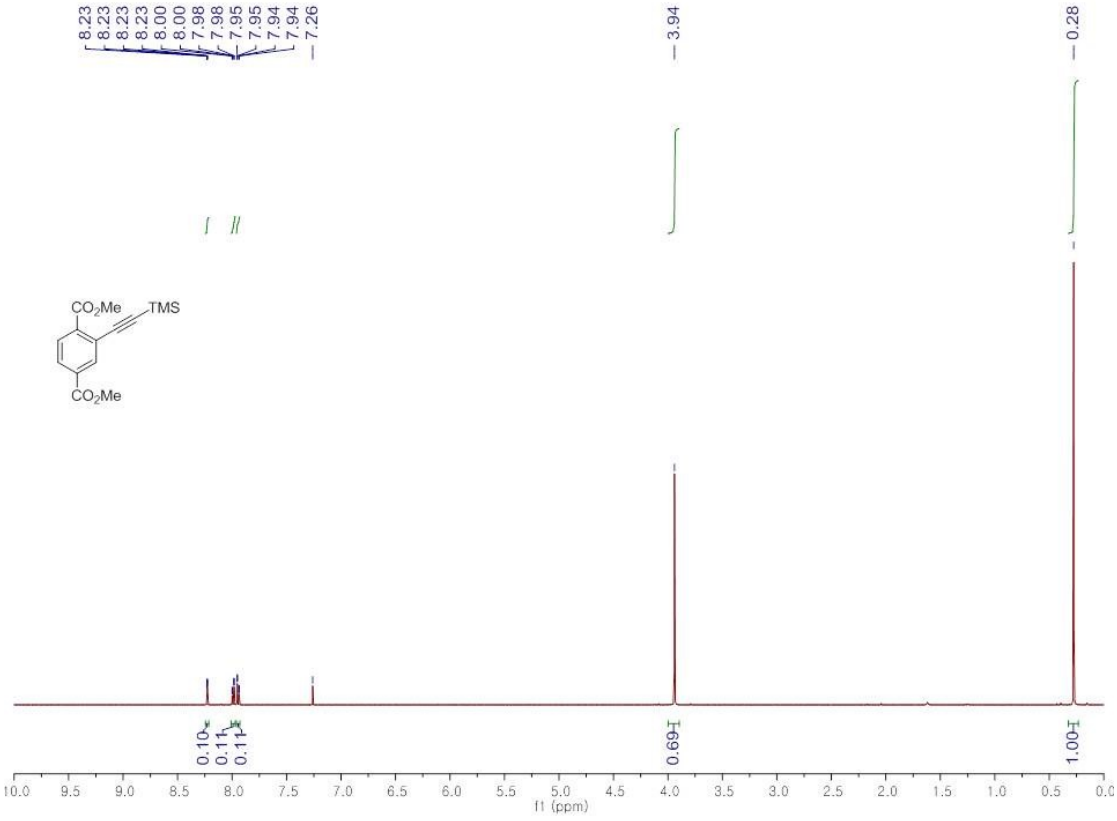
^{1}H NMR and ^{13}C NMR spectra of the synthesized organic compounds

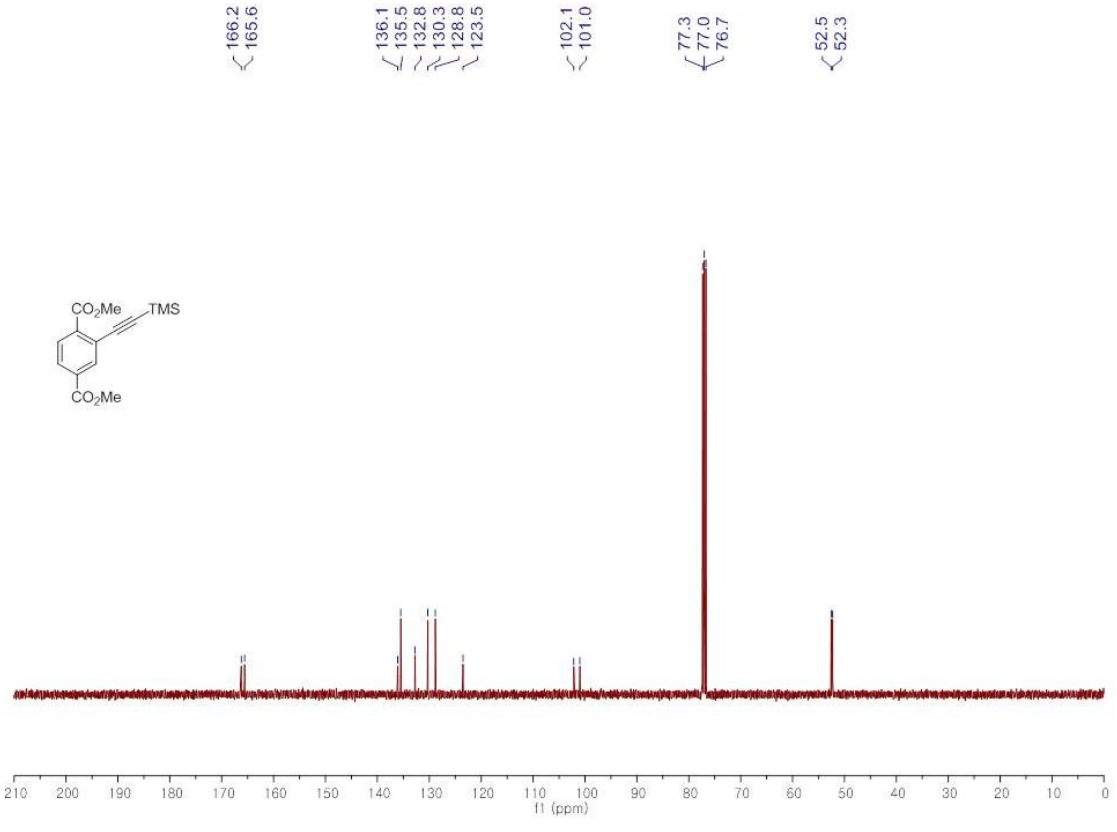
BDCE-Br


8.31
8.31
8.01
8.01
7.99
7.99
7.82
7.80
3.95
3.94
CO2Me
Br
CO2Me
0.91
0.97
0.96
6.00
f1 (ppm)

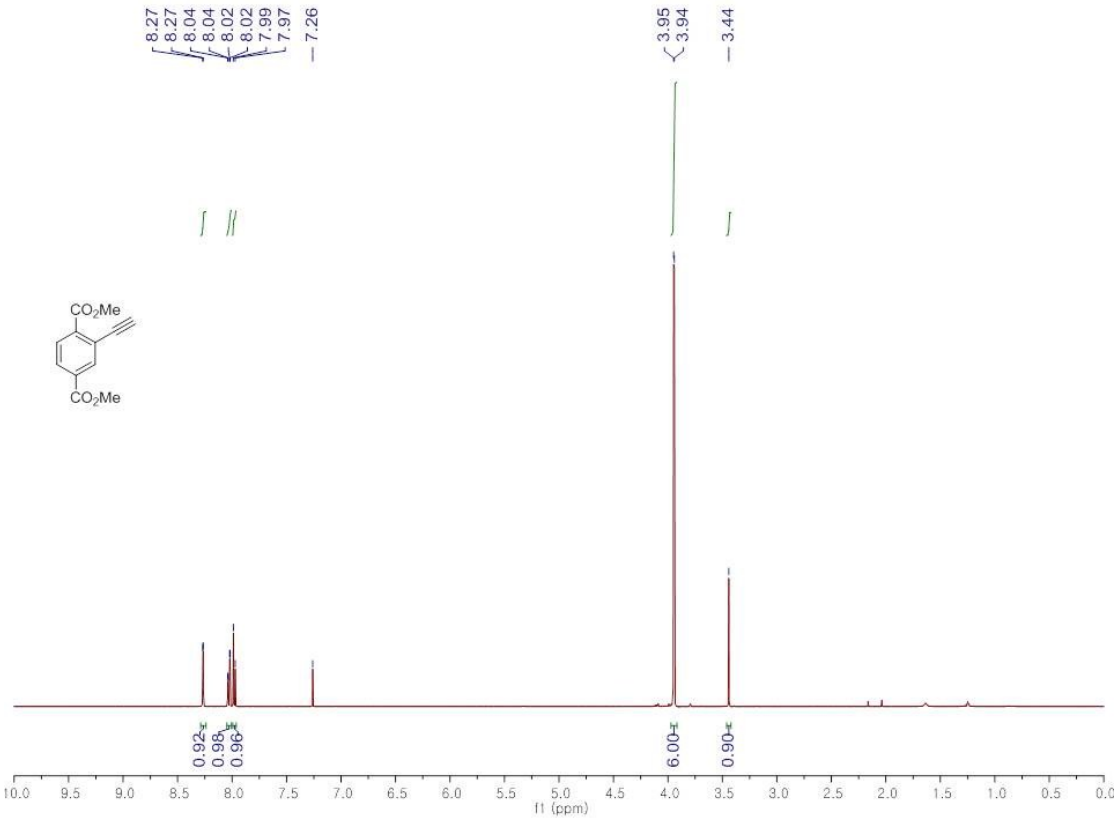

166.1
165.0
136.1
135.2
133.7
131.0
128.1
121.4
77.3
77.0
76.7
52.8
52.7
CO2Me
Br
CO2Me
f1 (ppm)

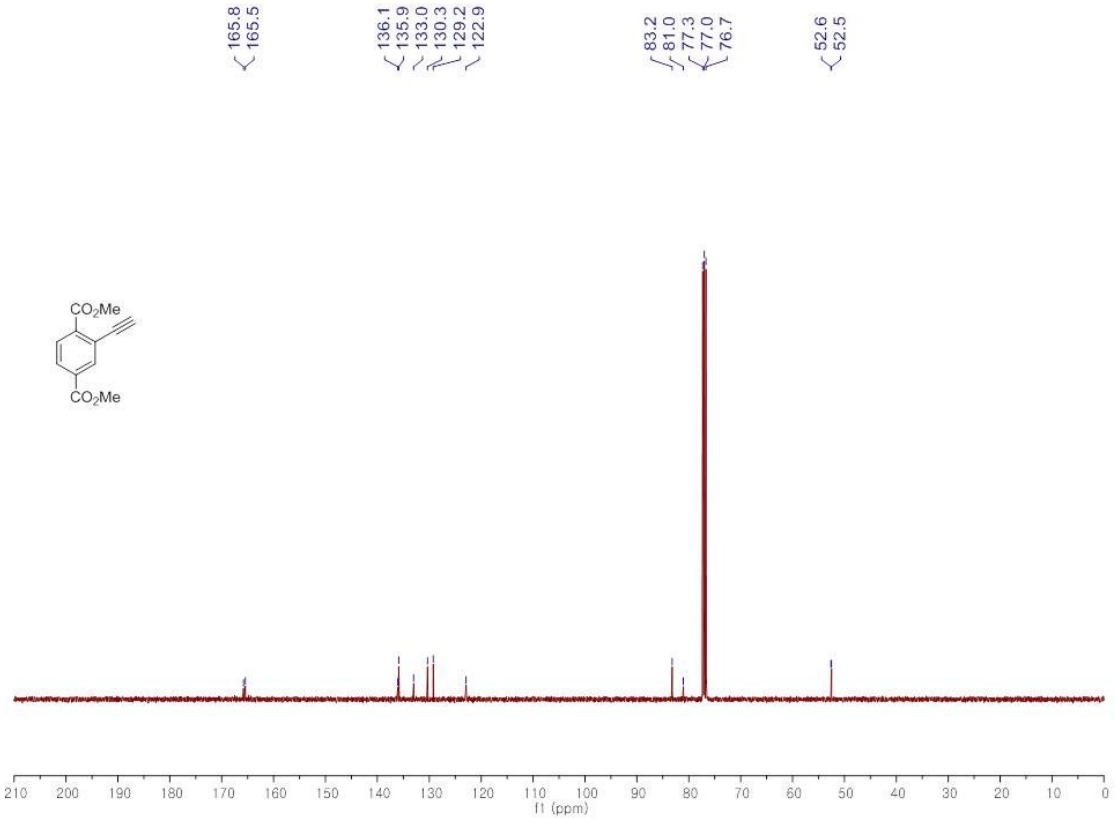
BDCE-TMS-ethynyl



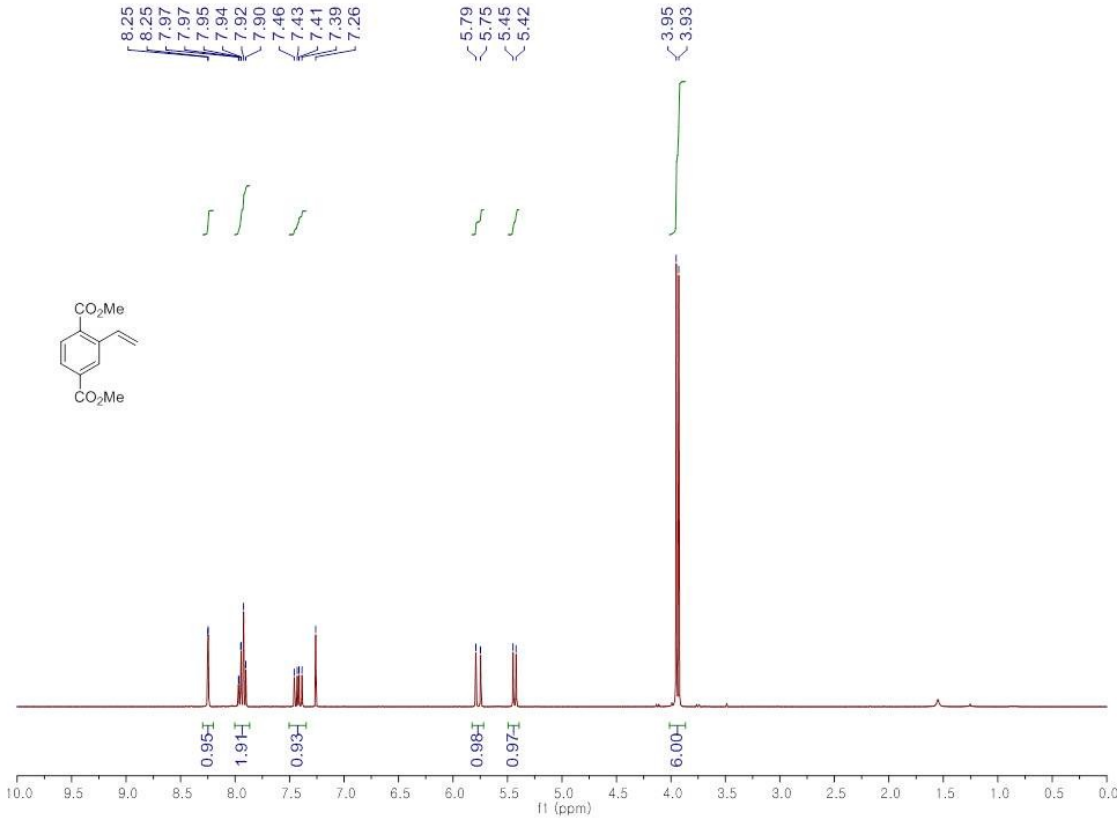


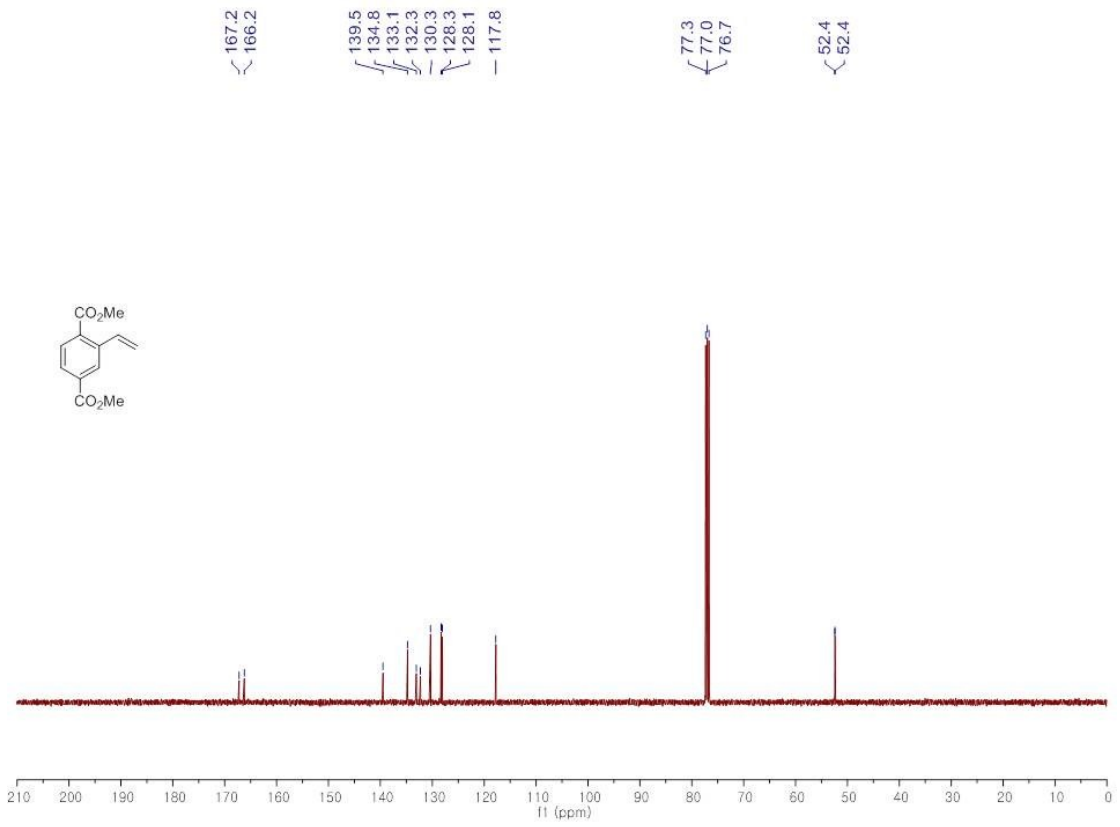
BDCE-ethynyl



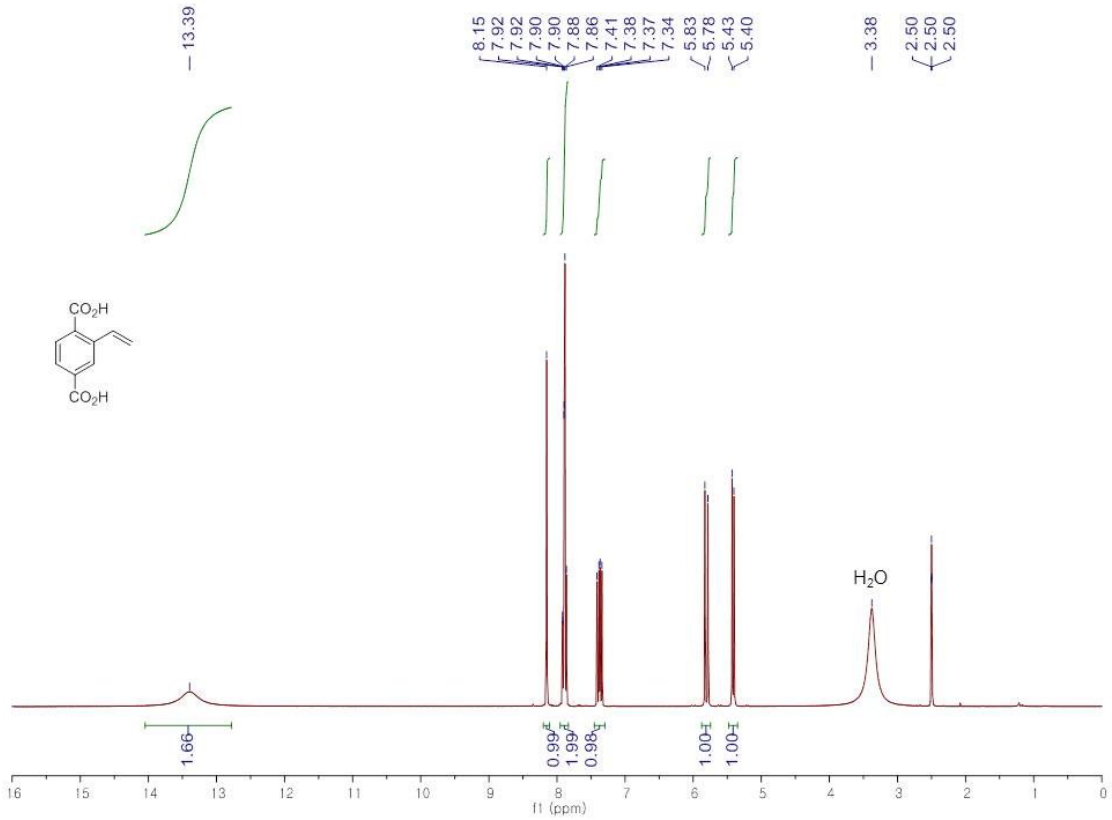


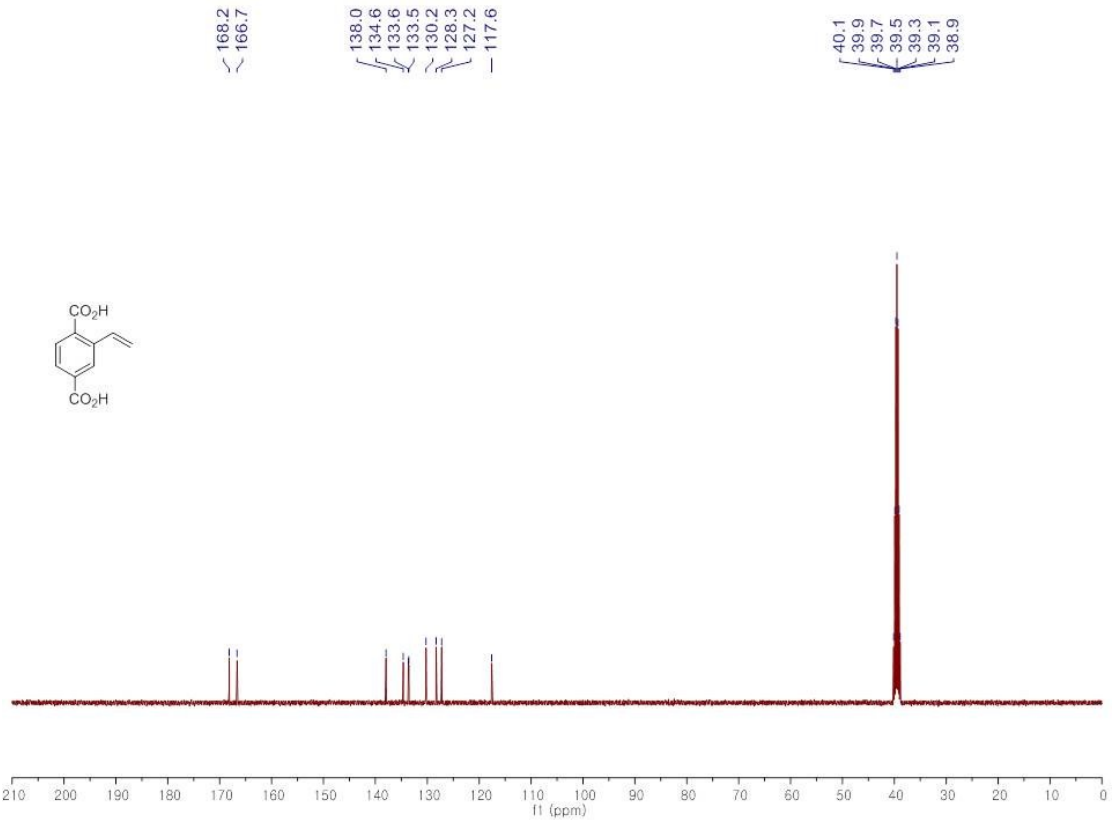
BDCE-vinyl


8.25
8.25
7.97
7.97
7.95
7.94
7.92
7.90
7.46
7.43
7.41
7.39
7.26
5.79
5.75
5.45
5.42
3.95
3.93
CO2Me
CO2Me
0.95
1.91
0.93
0.98
0.97
6.00
f1 (ppm)


167.2
166.2
139.5
134.8
133.1
132.3
130.3
128.3
128.1
117.8
77.3
77.0
76.7
52.4
52.4
CO2Me
CO2Me
f1 (ppm)

BDC-vinyl


13.39
8.15
7.92
7.92
7.90
7.90
7.88
7.86
7.41
7.38
7.37
7.34
5.83
5.78
5.43
5.40
3.38
2.50
2.50
2.50
CO2H
CO2H
H2O
1.66
0.99
1.99
0.98
1.00
1.00
f1 (ppm)


168.2
166.7
138.0
134.6
133.6
133.5
130.2
128.3
127.2
117.6
40.1
39.9
39.7
39.5
39.3
39.1
38.9
CO2H
CO2H
f1 (ppm)